



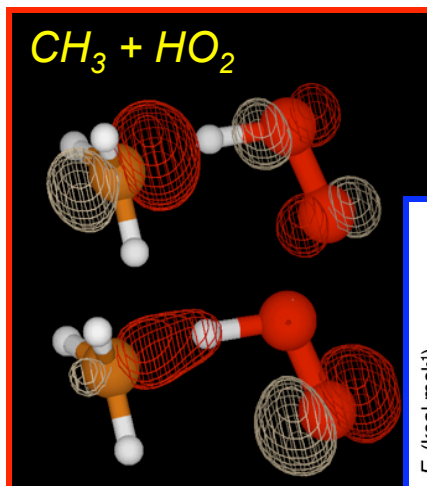
Combustion Chemistry Group Theory and Modeling

Ahren Jasper, Judit Zádor, and Jim Miller

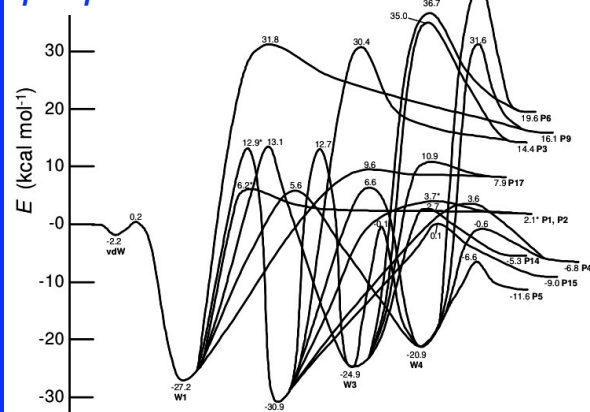
Predictive Chemical Kinetics

Methods

- High-level quantum chemistry
- Transition state theory development
- Master equation analysis
- Experimental validation
- Inform detailed reaction mechanisms

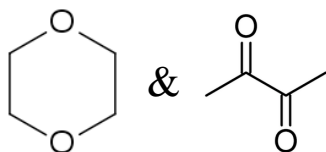


propene + OH

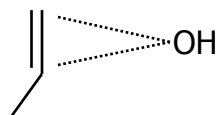


Recent applications

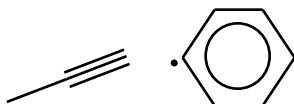
- 1,4-dioxane, diacetyl, halogenated precursor, etc., decompositions (exp: **Tranter**, **ANL**)



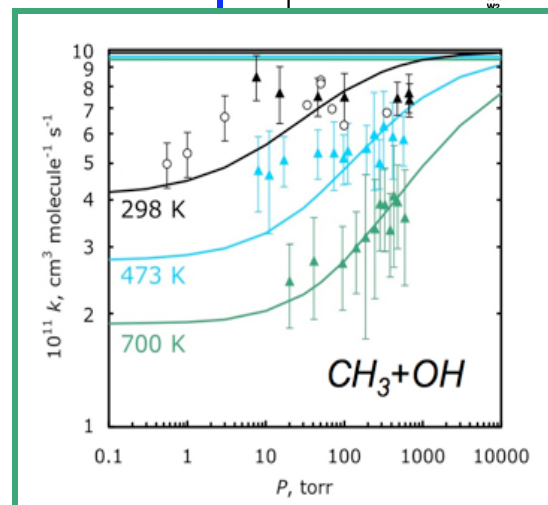
- propene + OH (exp: **Taatjes**, **Sheps**)



- phenyl + propargyl (exp: **Osborn**)



- $CH_3 + X$, $CH_2 + X$; $X = OH$, HO_2 , halogens
- Butanol, Propane, DME, etc.



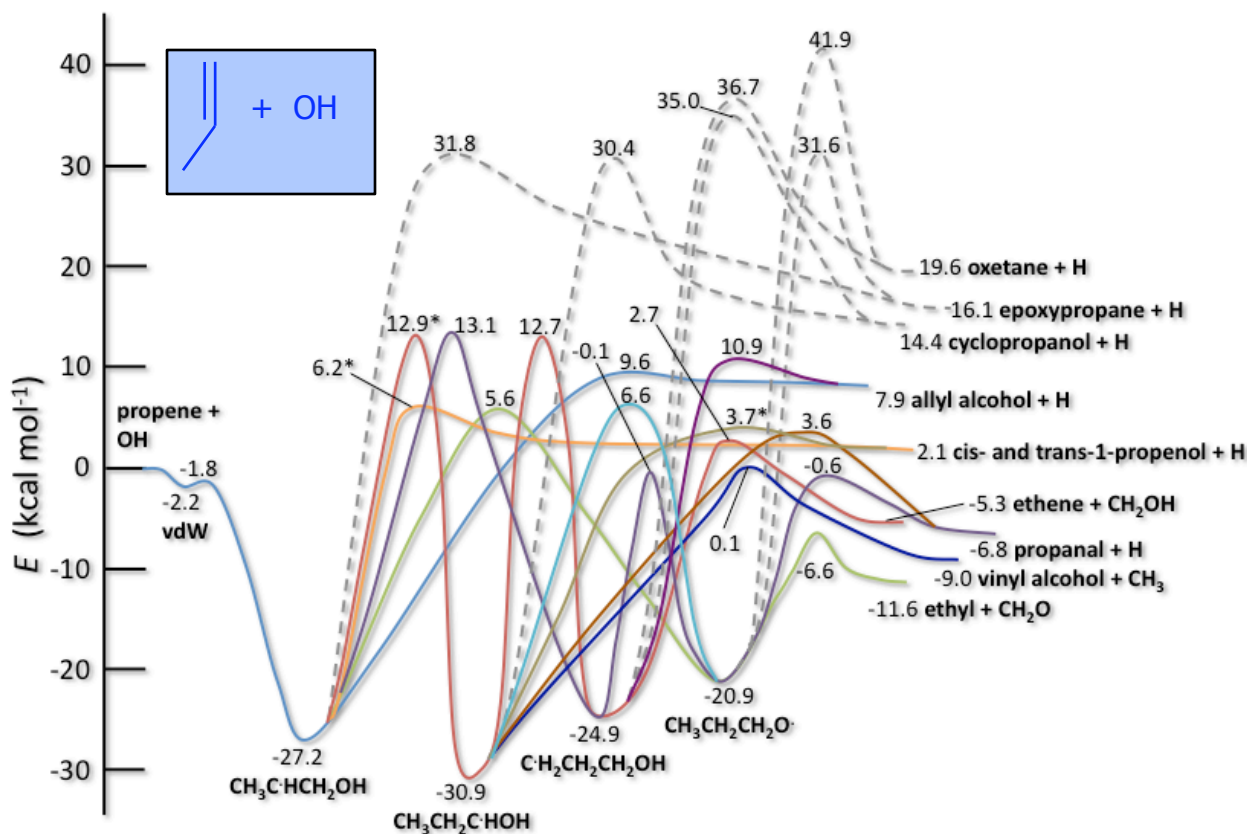


High-level quantum chemistry

Automated PES exploration (NEW)

One major bottleneck to predictive chemical kinetics calculations is the large human effort required to explore complicated potential energy surfaces. We are developing automated searching procedures.

Judit Zádor, Early Career LDRD



Theoretical uncertainties

We are validating & quantifying the errors in our q.c. approaches, with an emphasis on quantifying how this uncertainty propagates into the predicted kinetics.

Direct dynamics

We are developing strategies for coupling our dynamics codes directly with q.c. codes, often relying on high performance DOE and SNL computing resources.

Barrierless Kinetics

“Loose” transition states

Extended fragment separations

Low-frequency motions

Highly anharmonic

VRC-TST approach

Monte Carlo sampling over relative orientation

Frozen fragment geometries

Adiabatic vibrations

Remaining d.o.f.

+ *Fully dimensional*

+ *Fully coupled, anharmonic*

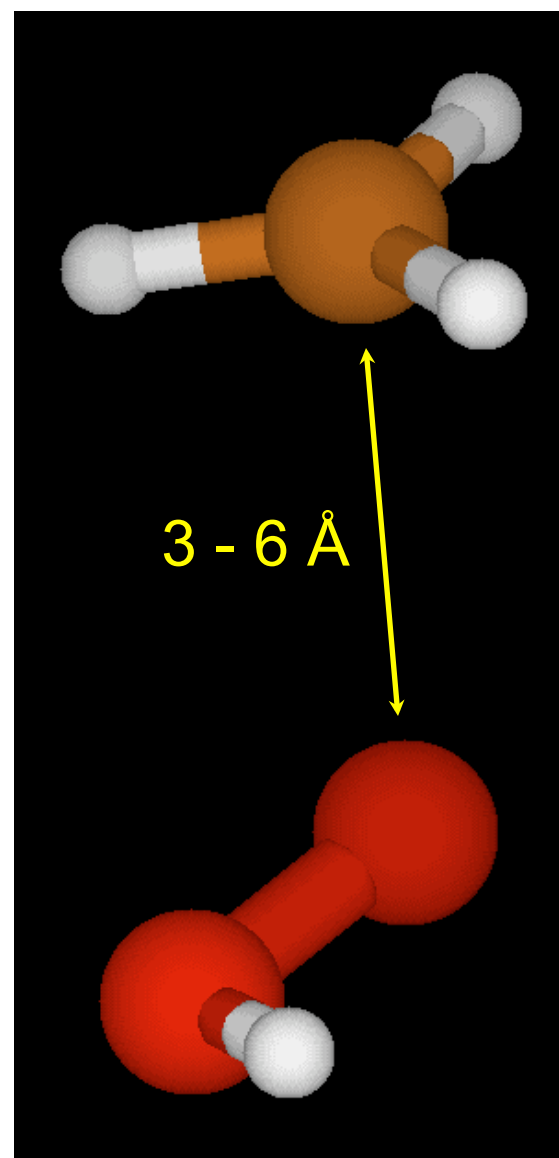
– *Classical fluxes*

Multireference electronic structure theory

Validated for many radical-radical reactions

Typical errors < 25%

**Software: VaReCoF, Yuri Georgievskii
and Stephen Klippenstein**





E.g.: $\text{CH}_3 + \text{OH}$, a well-studied system

Experimental (symbols)

- $T = 298 \text{ K}$
 - 5: $k = 7\text{--}10 \times 10^{-11} \text{ cm}^3/\text{s}$
 - 2: higher
- $T > 298 \text{ K}$
 - 2: $k \propto T^0$
 - 1: $k \propto T^{-n}$

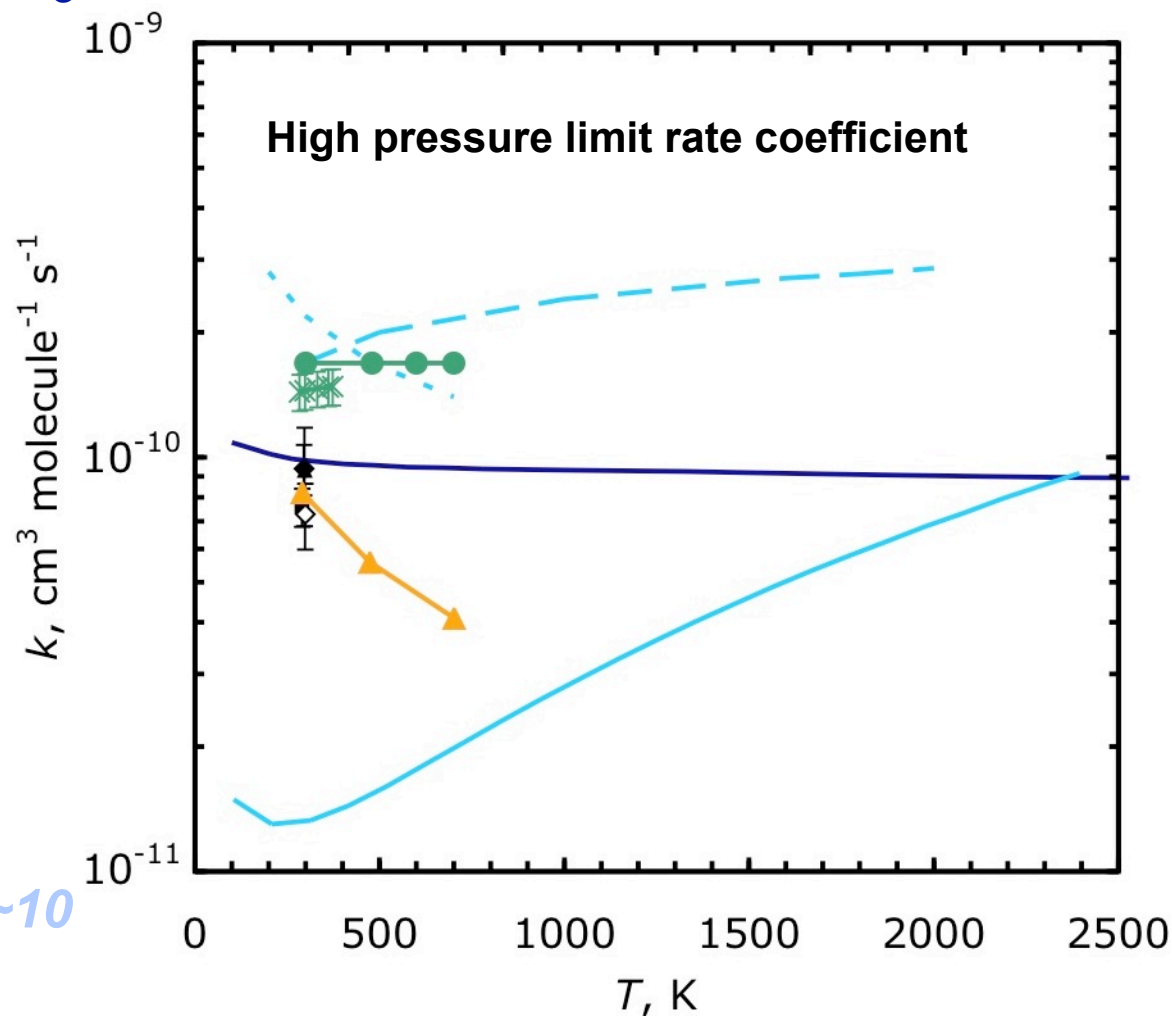
Theoretical (blue lines)

- Previous theory

*Rates vary by a factor of ~10
Different T -dependences*

- Present theory

Good agreement at 298 K
Very little T -dependence



- | | |
|------------------------------------|-------------------------|
| ▲ Sworski et al. (1980) | — Jordan et al. (1991) |
| ◆ Anastasi et al. (1991) | - - - Xia et al. (2001) |
| ■ Hughes et al. (1992) | — Ing et al. (2003) |
| ◇ Deters et al. (1998) | |
| ● Oser et al. (1992) | |
| × Fagerstrom et al. (1993) | |
| ▲ De Avillez Pereira et al. (1997) | |



$\text{CH}_3 + \text{OH}$: Falloff

Experimental falloff

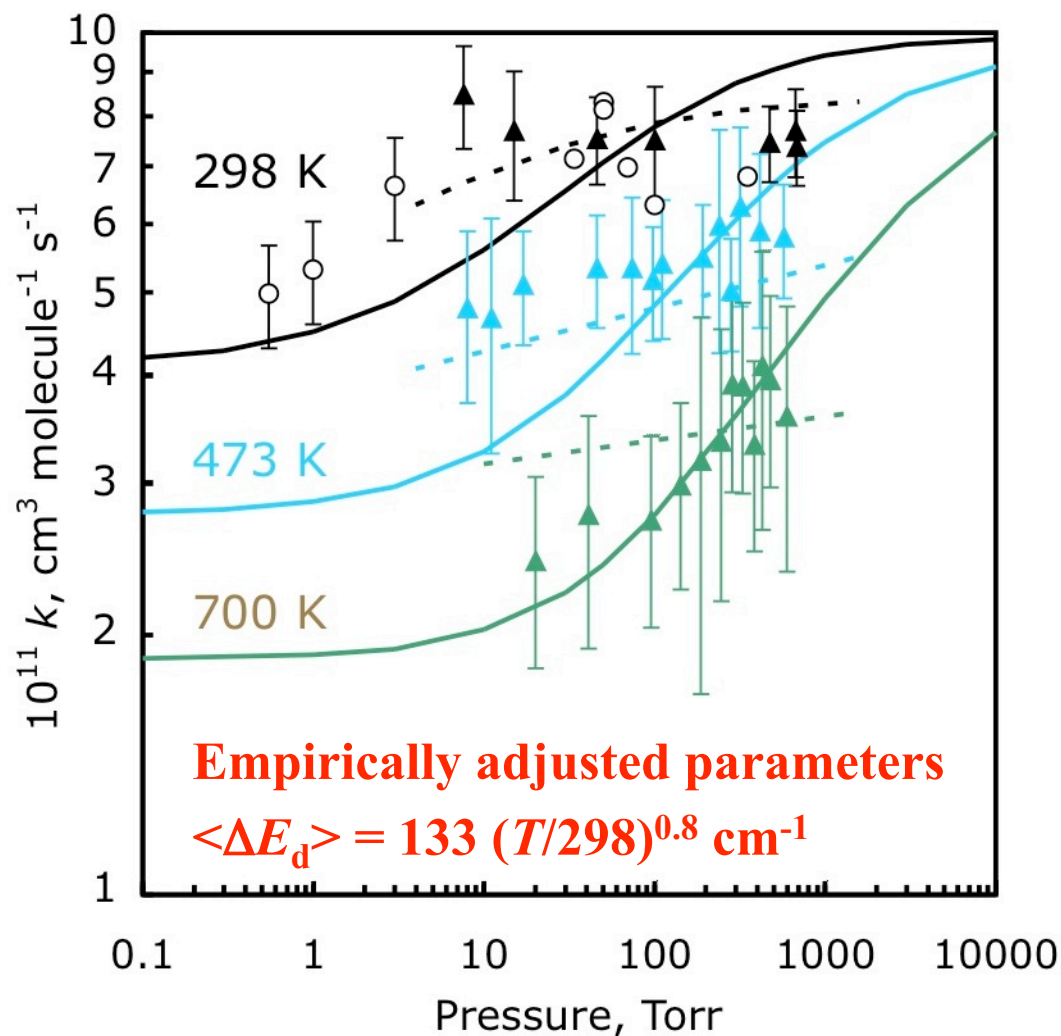
Measured (symbols)

Fits (dotted lines)

- Minor pressure dependence
- Strong high P T -dependence

Our theory (solid lines)

- Stronger P dependence
- Less T dependence at high P

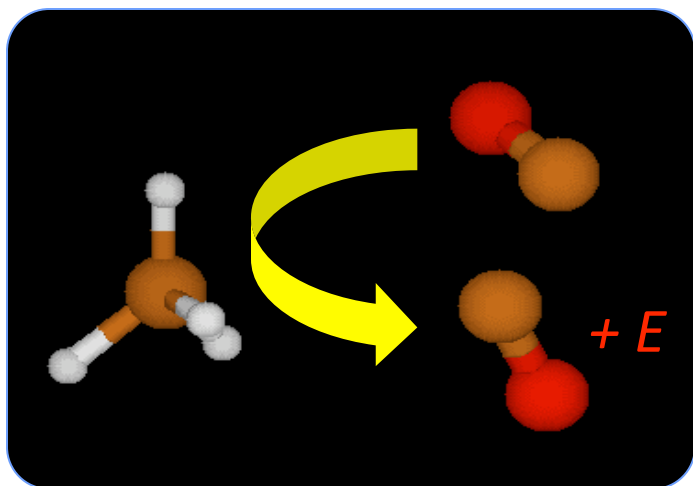


Triangles: De Avillez Pereira, Baulch, Pilling, Robertson, and Zeng, *J. Phys. Chem. A* **1997**, 101, 9681.

Dotted: De Avillez Pereira et al. master equation analysis

Circles: Deters, Otting, Wagner, Temps, László, Dóbé, Bérces, *Ber. Bunsenges. Phys. Chem.* **1998**, 110, 2080.

Predictive Energy Transfer Calculations



Direct Classical Trajectories

- **Goal:** Enable predictive calculations of $k(T,p)$
- **Background:** Almost exclusively empirical treatments
- **New:** Initial conditions consistent with the master equation
 - Full dimensional *ab initio* PESs
 - Improved sampling, massively parallel architectures

Systems



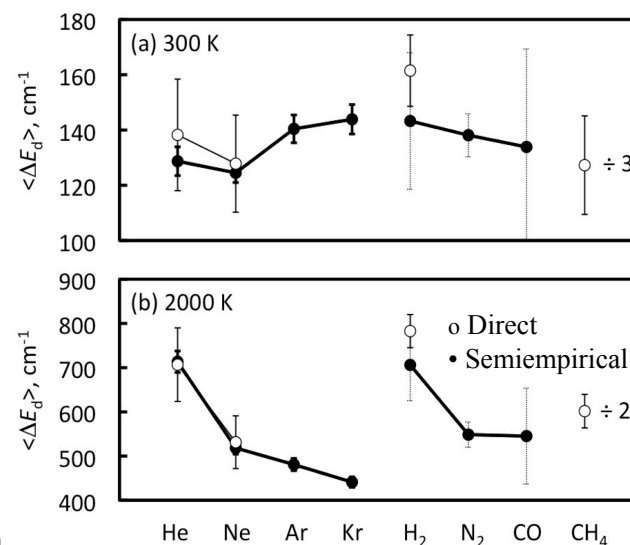
- Quantify errors associated with approximate PESs
- Test kinetics against experiment for He, Ar, Kr, CH_4



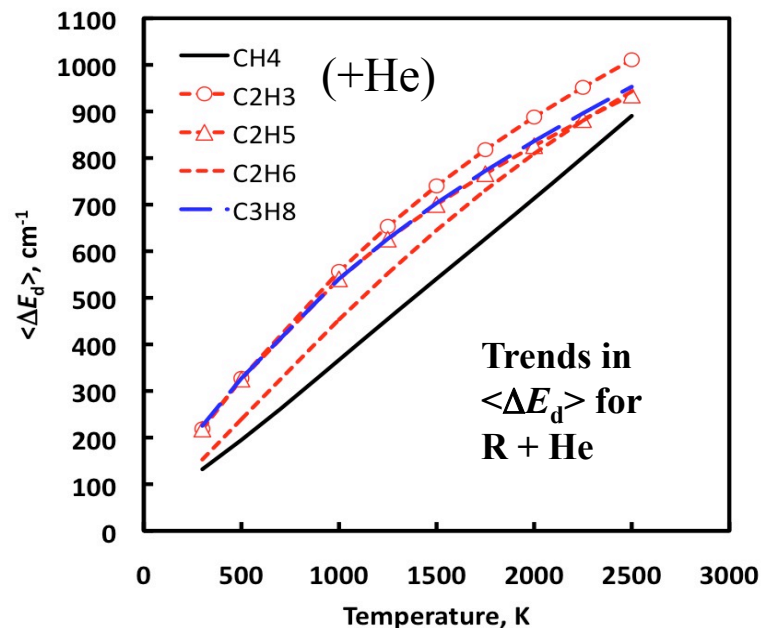
- Effect of weaker bonds on accuracy of direct trajectories



- Effect of multiple dissociation channels
- Look for trends to develop predictive models



Trends in
 $\langle \Delta E_d \rangle$ for
 $\text{CH}_4 + \text{M}$



Trends in
 $\langle \Delta E_d \rangle$ for
 $\text{R} + \text{He}$

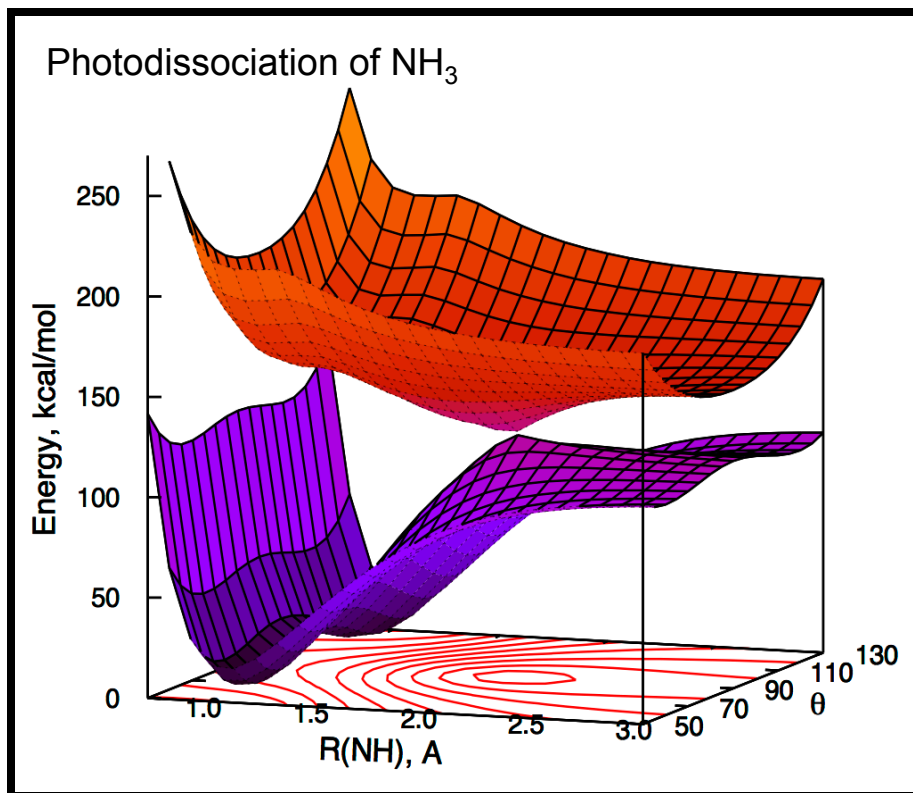
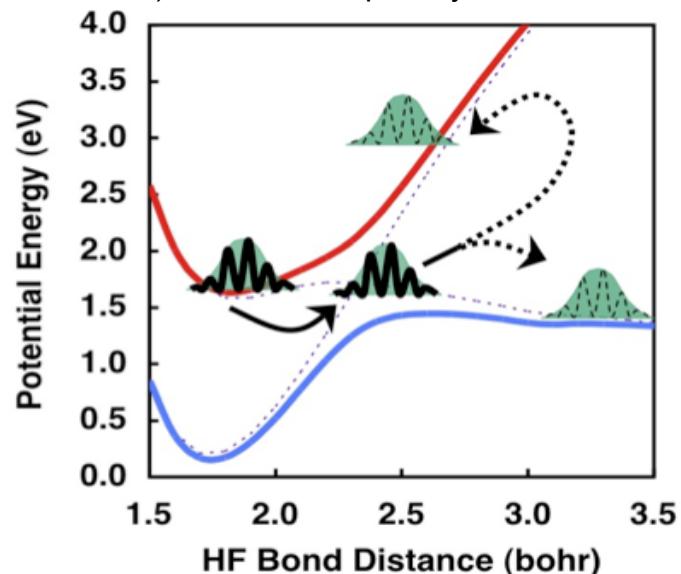
Non-Born–Oppenheimer Chemistry

Multistate molecular dynamics and transition state theory

- **DiNT computer code for NBO MD**
Direct methods (Molpro, Gaussian, etc)
Surface hopping and decay-of-mixing
Electronic coherence and decoherence

New challenges in multistate MD

Coherent (solid arrow) and decoherent (dashed arrows) motion in coupled systems



Applications

- Photodissociation of NH₃, Na...FH, HBr, CH₃X
- Spin-forbidden processes in combustion
O(³P) addition to singlet hydrocarbons
H + HO₂, H+NCO, etc
- Use NBO MD to develop NBO TST



- Informed by predictive kinetics and experiments
- NO_x chemistry
- Aromatics/PAH/soot formation
- Experimental validation and interpretation (Hansen et al.)
- Chemkin
- Modeling by Jim Miller and Nils Hansen

